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**IPST Technical Paper Series Number 902**

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May 2001

Submitted to  
Journal of Pulp and Paper Science  
and  
11th International Symposium on Wood and Pulping Chemistry  
(ISWPC)  
Nice, France  
June 11-14, 2001

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# THE FATE OF HEXENURONIC ACID GROUPS DURING ALKALINE PULPING OF LOBLOLLY PINE

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## ABSTRACT

This study conducted detailed characterizations of HexA content in softwood pulps obtained in various alkaline wood pulping processes and conditions. The study found that the maximum HexA formation rate is linearly dependent on hydroxide ion (effective alkali) concentration and the rates of HexA formation and degradation reactions are not affected by the presence of sulfide or AQ. The study also found that the amount of HexA in pulp from one-stage cooking is directly related to the amount of effective alkali (EA) consumed, regardless of the pulping processes and conditions. Furthermore, the same maximum amount of HexA was found in various pulps obtained from different pulping processes for a given wood species.

## INTRODUCTION

The formation of hexenuronic acid groups (HexA) during alkaline wood pulping has recently become a concern in the pulp industry because of its detrimental effects on bleaching operations, such as increased consumption of bleaching chemical, bonding with transition metals, and a reduced ceiling for pulp brightness. Thus, research in this area has been very active in the last several years. One area of research is developing analytical methods to determine HexA content [1-6], which will assist the studies on the issues related to HexA that lead to the control of bleaching plant operations. The other two areas are developing HexA-removal processes prior to bleach plant [1] and understanding the impact of HexA on different bleaching stages and sequences [7-9]. However, there have been few reports of research on the effect of various parameters, including alkali charge, temperature, pulping time, wood species, pulp yield, and pulping additives (AQ and polysulfide), on HexA formation. Such information is critically needed for demonstrating the feasibilities of HexA removal during kraft cooking.

Although a number of studies have reported that the HexA content in pulp is a strong function of the pulping process [10-11], few studies have reported on the effects of pulping parameters on the formation of HexA [12-13]. Buchert et al. [13] studied the effect of two parameters, cooking time and alkali charge, on HexA formation using a limited amount (12-36%) of pulp xylan peeled by xylanase. They found that the maximum amount of HexA was formed at the end of the heating-up period, and the HexA content was reduced by over 50% when active alkali charge was increased from 18 to 22%. More recently, Gustavsson et al. [14] reported that the HexA content at kappa number of 20 in Scotch pine pulp

could be predicted as a function of cooking time, initial [HS<sup>-</sup>] and [HO<sup>-</sup>]. They found that HexA formation is increased with the increase of initial sulfide concentration and the decrease of initial NaOH concentration. Furthermore, they found that the effect of cooking time was negligible, i.e., only to the power of 0.06. These two studies [13, 14] were conducted using high liquor-to-wood ratio, 6:1, and two-stage cooking with fresh liquors in each stage, conditions that have limited applications in conventional pulping processes.

Recently, Tenkanen et al. [15] presented a detailed comparison of three HexA measurement methods [1,3,5]. In general the three methods can give consistent measurements of HexA. However, all three methods are tedious and time-consuming (all take several hours to complete one measurement), which is probably why a systematic study on HexA formation in various pulping processes has not been conducted. In this study, a detailed characterization of HexA in chemical pulps obtained during various pulping processes was conducted using a simple and rapid method [16] that we developed. The impacts of effective alkali (EA) charge, EA consumption, pulping process, and addition of AQ on time-dependent HexA content in pulp were investigated. The relationship between HexA content, pulp kappa number, and yield was also analyzed. The HexA content was also quantitatively correlated with methanol content in the corresponding pulping liquor.

## EXPERIMENTAL

### Pulping

All pulping experiments were carried out in 500-mL bomb digesters. Eight bombs were mounted on a rotating drum and heated with glycol oil. Fifty grams (ODW) of loblolly pine chips were charged in each bomb. Soda cookings with active alkali charge of AA=18%, low-sulfidity cookings of S=15% with AA=15%, and high-sulfidity cookings of S=30% and AA=18% were conducted. Liquor-to-wood ratio was 4:1. The cooking temperature was ramped at 2.1°C/min from 23°C for 70 minutes and then maintained at 170°C. Cooking time was varied for a set of digestions in different bombs conducted under the same pulping condition to obtain time-dependent formation data of HexA and methanol. The pulp was completely disintegrated in a laboratory blender and thoroughly washed with tap water in a basket with 200-mesh screen. Pulp pads were then prepared in a handsheet machine for the measurement of pulp yields, kappa numbers, and HexA. The pulp yield, kappa number, and chemical strength of the cooking liquor, such as EA and sulfidity, were measured according to standard TAPPI test methods [17].

### Measurement of HexA in Chemical Pulps

In a previous study [16], we developed a reliable, simple, and rapid technique for HexA measurements in chemical pulps that is particularly suitable for the present systematic study. In this method, 22 mmol/L (0.6 %) mercuric chloride and 0.7 % sodium acetate were used to make a hydrolysis solution. The mercuric chloride (HgCl<sub>2</sub>) and sodium acetate trihydrate (CH<sub>3</sub>COONa·3H<sub>2</sub>O) of analytical grade were from



formation from wood degradation in the early stage of pulping. The measurements indicated rapid release of methanol, and the amount of methanol formed was about 28 mmol/kg-OD wood, very close to the methanol intercept of 32 mmol/kg-OD wood shown in Fig. 2.

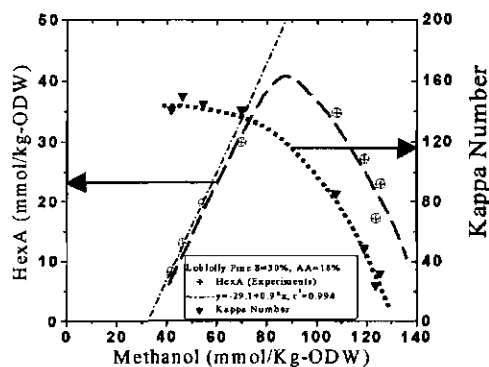


Fig. 2. The correlation of HexA in pulp to the methanol measured in pulping liquor during the initial stage of conventional kraft pulping of loblolly pine.

### Effect of Effective Alkali Charge on HexA Formation

Figure 3 shows the time-dependent HexA formation in different pulping processes. The data clearly show that the addition of AQ does not affect the formation and degradation of HexA. Although the profiles for HexA in various pulps obtained in different pulping conditions (soda and kraft with low and high active alkali charge and different sulfidities) are quite different, the same maximum amount of about 65 mmol/kg-OD pulp of HexA was yielded during all the pulping processes after the pulping temperature reached 170°C. The cooking time required at the maximum cooking temperature to reach the maximum HexA value varies with cooking process from 10, 20, and 30 min for soda (AA=18%), high AA (18%) and sulfidity (30%), and low AA (15%) and sulfidity (15%) kraft pulping, respectively. Clayton [19] found that Reaction (1) is very rapid and about 90% of the methoxyl groups on 4-O-methylglucuronoxylan were removed to form HexA after 25 minutes of the reaction at 170°C, which illustrates that the final amount of HexA formed does not vary with pulping process for a given wood species.

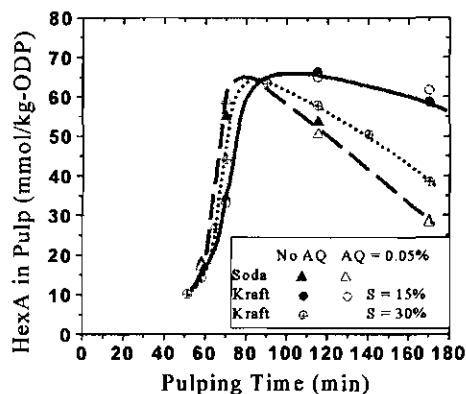


Fig. 3. Time-dependent HexA in pulps during various pulping processes with and without AQ addition.

According to Reaction (1), the HexA formation rate can be written as follows:

$$\frac{d[\text{HexA}]}{dt} = k \cdot \text{Exp}(-E_a / RT) \cdot [(\text{OCH}_3)_{\text{-xylan}}][\text{OH}^-] \quad (2).$$

Therefore, the effective alkali (EA or OH<sup>-</sup> concentration) is a key factor controlling the formation of HexA for a given cooking temperature and wood species. Figure 4 shows that the maximum HexA formation rate is linearly proportional to the initial EA concentration in the cooking liquors or the first order in hydroxide ion concentration. Data also clearly show that a higher initial EA leads to faster HexA formation.

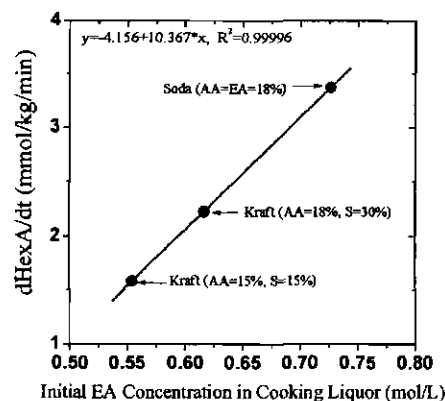


Fig. 4. Effect of initial EA concentration on the maximum formation rate of HexA in various pulping processes.

An interesting phenomenon was found when we plotted the HexA content vs. the consumption of EA. As shown in Fig. 5, HexA profiles for different pulping processes fall to a single curve. Although a quantitative interpretation of this result is not presently possible, a few implications can be drawn from it. Firstly, the fate of HexA in pulp, both formation and reduction, is only a function of hydroxide ion. Secondly, all the reactions during pulping that consume a major part of the hydroxide proceed to the same degree as that of reactions associated with formation or reduction of HexA in all pulping processes. It is known that the hydroxide is mainly consumed in the neutralization of organic acid groups in original wood components, and that the acids are generated during degradation of carbohydrates and lignin. Gustavsson et al. [14] concluded that the HexA content in pulp when normalized by the xylan content in the pulp depends on initial HS<sup>-</sup> concentration. However, the results in Fig. 5 clearly indicate that both formation and dissolution of HexA are only affected by the amount of alkali consumed and not by sulfide. We believe that the normalization by the xylan content in the pulp complicates the understanding of key variables affecting HexA content. Eq. (2) clearly indicates that HexA formation will only be affected by alkali charge. We found that the HexA data (without normalization) of Gustavsson et al. [14] correlate to their consumed EA very well with a nonlinear relationship very similar to the right part of our curve shown in Fig. 5, further confirming our conclusion.

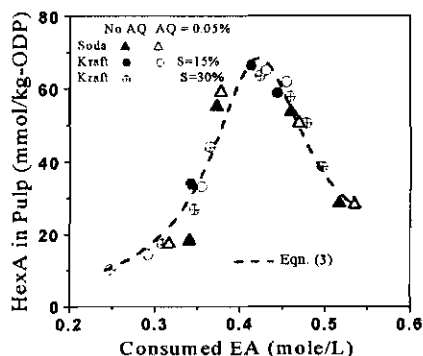


Fig. 5. The relationship between HexA content in pulp and the corresponding EA consumption.

The results in Fig. 5 can be used to estimate the amount of HexA content in pulp using EA data without conducting HexA measurements. If one can determine the amount of EA consumed for any type of one-stage cook, e.g., kraft with different sulfidity, soda, with AQ, and without AQ, one can determine the amount of HexA in pulp using the data shown in Figure 5 without conducting HexA measurements. To facilitate this estimation, we conducted a least-squares fit of the data to obtain the following equation for HexA determination:

$$\text{HexA} = \frac{a \cdot w}{5(EA_{\text{consum}} - 0.42)^2 + w^2} + b(EA_{\text{consum}})^2 \quad (3)$$

where  $a = 9.1$ ,  $w = 0.15$ , and  $b = 43$ . Eq. (3) is purely a mathematical fit of the data and specific for loblolly pine. Eq. (3) fits the data well, particularly at a high level of EA consumption as shown in Fig. 5. But the accuracy of Eq. (3) decreases outside the region where there are no experimental data points.

The data shown in Fig. 5 were obtained in the pulping of loblolly pine. The profile of HexA vs. EA consumed may be different for different wood species. The validity of the results in Fig. 5 and Eq. (3) for other wood species will have to be investigated in the future. Furthermore, the results in Fig. 5 were obtained in a one-stage pulping process, i.e., no liquor exchange or addition during cooking. The validity of the results in Fig. 5 and Eq. (3) for complex pulping processes, such as EMCC and RDH, will also be investigated in the future. In these complex processes, determination of EA consumption may require a lot more effort than just simply determining HexA in pulp. Therefore, the practical importance of Fig. 5 may be limited because the measurement of HexA will be easier than the determination of EA consumption.

#### Relationship of HexA Content in Pulp with Kappa Number and Yield

Because HexA formation through hydrolysis and reduction proceed simultaneously with delignification, correlating HexA with pulp number may have some practical applications. We plotted the HexA formation as a function of pulp kappa number and yield for both soda and kraft cooks with or without AQ as shown in Figs. 6 and 7, respectively. The residual effective alkali concentrations in the black liquors at the end of the cook are 7.5 for high-sulfidity (30%), 7.1 and 6.5 for low-

sulfidity (15%) kraft pulping with and without AQ, respectively, and 12.9 and 11.9 g/L for soda pulping with and without AQ, respectively. HexA content in pulps with AQ addition is slightly higher than that in pulp without AQ addition. These results do not contradict the findings presented in the previous section, i.e., HexA formation is mainly affected by hydroxide ion concentrations, not by the presence of AQ or sulfide. However, the addition of AQ facilitates delignification and thus reduces the required pulping time, which results in a high yield of HexA. The results shown in Figs. 6 and 7 clearly demonstrate that sulfidity has no effect on HexA formation and degradation.

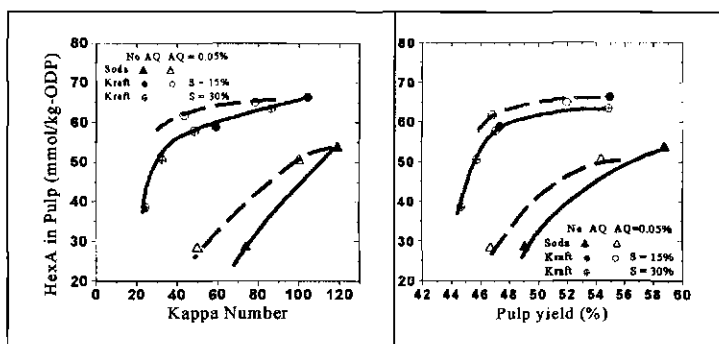


Fig. 6. The relationship between HexA content in pulp and the corresponding kappa number and pulp yield.

For a given pulp kappa number or yield, HexA in kraft pulp is much higher than that in soda pulp as shown in Fig. 6. The difference in HexA content between soda and kraft pulp at a given yield cannot be explained by the negative effect of higher hydroxide concentration on pulp yield; it can only be attributed to the fact that hydroxide concentration has a much stronger effect on HexA reduction than on pulp yield. The difference between HexA content in soda and kraft pulps at a given kappa number is due to the difference in delignification selectivity. Kraft cooking not only has lower EA concentration at the same active alkali charge, but also requires a much lower H factor to reach a given kappa number. Both lower H factor and EA concentration will result in less HexA degradation.

#### CONCLUSION

We conducted detailed characterizations of HexA content in softwood pulps obtained in various alkaline wood pulping processes and conditions. Our study found that the maximum HexA formation rate is linearly dependent on (first order) hydroxide ion (effective alkali) concentration, and the rates of HexA formation and reduction are not affected by the presence of sulfide or AQ. The study also found that the amount of HexA in pulp from one-stage cooking is directly related to the amount of EA consumed, regardless of the pulping processes and conditions. Furthermore, the same maximum amount of HexA was found in various pulps obtained from different pulping processes for a given wood species, regardless of the pulping processes and conditions. HexA content as a given yield or kappa number was different at different sulfidity or AQ addition, which is a result of the increased delignification rate by

these additives. Finally, the study demonstrates a linear relationship with unity slope between the amounts of HexA in the pulps obtained in the initial stage of pulping and the amounts of methanol found in the corresponding pulping liquors, which indicates that HexA reduction due to xylan dissolution and methanol formation by lignin demethylation are negligible in the initial stage of pulping and validates the accuracy of the technique for rapid HexA measurements that we developed [16].

## PRACTICAL IMPLICATIONS

Two possible practical implications could be derived from the information generated from this study. The first one is that the HexA content in pulp could be estimated by knowing the EA consumption of the cooking process for one-stage cooking. For multistage cooking processes, e.g., EMCC and RDH, the existence of the relationship has to be investigated in the future. The second implication is that finding suitable procedures or conditions to reduce HexA content during the pulping process is unlikely. This is because the amount of HexA removal is directly proportional to the EA consumption, but not to any other conditions. The amount of EA consumption is basically linked to the amount of carbohydrate degradation. Therefore, any attempts to reduce HexA during pulping will likely result in higher carbohydrate degradation, leading to lower yield and/or lower strength. Any improvement in delignification selectivity will lead to higher HexA content in pulp as is shown by the presence of sulfide and AQ. Finally, the HexA measurement method we developed [16] is not only simple and rapid (it only takes 30 minutes to obtain one measurement), but also accurate. Therefore, in practical applications, the method [16] has significant advantages over most of the existing techniques [1-6, 15], which all take several hours to obtain one measurement.

## ACKNOWLEDGEMENTS

This research was supported by the United States Department of Energy (Grant No. DE-FC07-96ID13438) and the State of Georgia (Grant No. PP99-MP9).

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